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(54) Title: PROCESS FOR PREPARING AN ALUMINA BOUND ZEOLITE CATALYST

(57) Abstract

In a process for preparing an alumina bound, zeolite catalyst, a zeolite of low silanol content is used as the source of zeolite used to prepare the catalyst. A particular zeolite used in this catalyst is zeolite Y. This catalyst may be combined with at least one hydrogenation component and used to hydrocrack hydrocarbons, such as gas oils. In particular, an NiW/USY/alumina catalyst may be used in a hydrocracking reaction to produce distillate boiling range hydrocarbons from higher boiling hydrocarbons.

PROCESS FOR PREPARING AN ALUMINA BOUND ZEOLITE CATALYST

This invention relates to a process for preparing an alumina bound, zeolite catalyst useful in hydrocracking hydrocarbons, such as gas oils.

5   Hydrocracking is a versatile petroleum refining process which enjoys widespread use in the refining industry. Hydrocracking has the ability to process a wide range of difficult feedstocks into a variety of desirable products. Feedstocks which may be treated by this process

10   include heavy naphthas, kerosenes, refractory catalytically cracked cycle stocks and high boiling virgin and coker gas oils. At high severities, hydrocracking can convert these materials to gasoline and lower boiling paraffins; lesser severities permit the higher boiling feedstocks to be

15   converted into lighter distillates such as diesel fuels and aviation kerosenes.

Hydrocracking is conventionally carried out at moderate temperatures of 350°C to 450°C (650°F to 850°F), because the thermodynamics of the hydrocracking process

20   become unfavorable at higher temperatures. In addition, high hydrogen pressures, usually at least 5600 kPa (800 psig) are required to prevent catalyst aging and so to maintain sufficient activity to enable the process to be operated with a fixed bed of catalyst for periods of one to

25   two years without the need for regeneration.

The catalysts used for hydrocracking usually comprise a transition metal such as nickel, cobalt, tungsten or molybdenum on an acidic support such as alumina or silica-alumina although noble metals such as platinum may also be

30   used. Combinations of metals such as nickel with tungsten have been found to be extremely effective with a wide variety of feedstocks as has the presulfiding technique which is now widely employed.

Hydrocracking processes using the hydrogen form of

35   zeolite Y as the acidic component are described, for example, in U.S. Pat. Nos. 3,269,934 and 3,524,809, and in

"Preparation of Catalysts III", ed. by G. Poncelet, P.
Grange, and P.A. Jacobs, Elsevier Science Publishers, 587
(1983).

High silica/alumina ratio zeolites have been shown to
be the preferred catalysts for many hydrocarbon upgrading
processes used petroleum refining and petrochemical
applications. These processes include hydrocracking (MPHC)
for maximum distillate production. It has, however, been
found that high silica zeolites typically exhibit an
increase in acid activity when bound with alumina.
Activation of the zeolite by the alumina binder has been
attributed to alumina incorporation into the zeolite
framework which decreases the silica/alumina ratio and
increases the zeolite acidity, as disclosed by C.D. Chang,
S.D. Hellring, J.N. Miale, K.D. Schmitt, P.W. Brigandi, and
E.L. Wu in J. Chem. Soc., Faraday Trans., I, 81, 2215
(1985).

In many cases this activation has a detrimental impact
on catalyst performance. For example, the performance of
VGO hydrocracking catalysts comprised of large-pore
zeolites disclosed in U.S. Pat. No. 4,820,402 demonstrates
a unique relationship between selectivity to high value
middle distillate products and increasing zeolite
silica/alumina ratio. Furthermore, the occurrence of
alumina binder activation in zeolites and the extent to
which it occurs have been difficult to predict.

Binding the zeolites with silica, as disclosed in U.S.
Pat. No. 4,582,815, is currently one of the preferred
methods of eliminating this binder activation. In some
applications, however, silica binding may not be applicable
such as with bi-functional hydrocracking catalysts where a
metal component must be dispersed on the binder. It would
be desirable, therefore, to develop a procedure for
preparing stable, l w acidity zeolites in alumina binder.

This present invention seeks to provide a process for the preparation of high silica zeolite catalysts with improved resistance to alumina binder activation.

Accordingly, the invention resides in a process for preparing an alumina bound zeolite catalyst, comprising the steps of:

(a)   starting with a zeolite which has a silanol content of less than 10%, expressed in terms of silicon atoms containing silanol groups vs. total silicon atoms;

(b)   mulling together alumina, said zeolite of step (a), and water to form an extrudable mass comprising an intimate mixture of alumina and said zeolite;

(c)   extruding the extrudable mass of step (b) to form a green strength extrudate; and

(d)   calcining the green strength extrudate of step (c) to increase the crush strength of the extrudate.

The invention further provides a process for hydrocracking a hydrocarbon feedstock, said process comprising contacting said feedstock and hydrogen with a hydrocracking catalyst comprising a hydrogenation component and an extrudate prepared according to the above-mentioned process.

The present invention provides a process for preparing zeolite catalysts that enables low acidity, high SiO_2/Al_2O_3 ratio zeolites to be stabilized toward increases in acid activity that arise from aluminum incorporation into the framework during the alumina binding procedure. The catalysts may be prepared from zeolites subjected to a thermal and/or hydrothermal treatment to reduce crystal defect sites, such as silanol groups, prior to contact with the alumina binder.

The procedure may involve a zeolite treatment, such as mild steaming, to effect a reduction in structural defect

sites within the zeolite, such as zeolite silanol groups,
prior to contact with the alumina binder.

Previous investigators have identified defect sites,
such as silanols, in high silica zeolites, such as ZSM-5,
5   using FT-IR and ^{29}Si MAS NMR as described by R.M. Dessau,
K.D. Schmitt, G.T. Kerr, G.L. Woolery, and L.B. Alemany in
J. Catal., 104, 484 (1987). Hydrothermal treatment reduces
the silanol content in ZSM-5 and this has been interpreted
to occur through a silanol annealing mechanism. However,
10   the relationship between zeolite silanol content and binder
activation, and the necessity to control zeolite silanol
content prior to contact with the alumina binder has
heretofore not been recognized.

The present process first involves combining alumina,
15   zeolite and water in a mulling procedure. The amount of
alumina should be sufficient to provide the required crush
strength to the ultimately produced extrudate and typically
will be 5-95 wt%, preferably 20-80 wt.%, on a 100% solids
basis. The amount of zeolite will be dependent on the
20   required catalytic activity to the ultimately produced
catalyst and again will typically be 5-95 wt%, preferably
20-80 wt.%, on a 100% solids basis. A sufficient amount of
water should be added to provide adequate extrudability to
the solids in the mixture. For example, the amount of
25   water may be 40-50 wt.% of the solids. This extrudable
mixture may be in the form of a paste.

The alumina which is used to form this extrudable
mixture may be in the form of a hydrated alumina, such as
pseudoboehmite.
30   The zeolite, which is used to form the extrudable mass
with alumina and water, has a low silanol content. This
silanol content may be less than 10%, e.g., less than 5%,
expressed in terms of silicon atoms containing silanol
groups vs. total silicon at ms. These percentages f
35   silanol content may be determined by ^{29}Si MAS NMR.
Silicon-29 NMR is an effective tool to determine the

silanol content. A ^{29}Si NMR spectrum of a high-silica
zeolite typically exhibits three Si species corresponding
to framework Si, silanol (SiOH), and diol (Si(OH)$_2$). By
integrating the areas of these peaks, the silanol content

5   can be determined. The method is described by E. Lippmaa,
M. Maegi, A. Samoson, M. Tarmamak, and G. Engelhardt in the
J. Am. Chem. Soc. 103, 4992, (1981). Other techniques that
can measure silanol content semi-quantitatively, including
FT-IR and proton NMR, can also be used.

10   It will be understood that, whenever the silanol
content of a zeolite is referred to herein, this silanol
content is attributed exclusively to silanols which are
part of the zeolite framework and excludes non-framework
silanols, such as those which may be present from amorphous

15   silica impurities and/or occlusions, e.g., carried over
from the reaction mixture used to prepare the zeolite.
Zeolites which may be used to form catalysts by
methods disclosed herein include medium-pore size and
large-pore size zeolites.

20   A convenient measure of the extent to which a zeolite
provides control of access to molecules of varying sizes to
its internal structure is the Constraint Index of the
zeolite. Zeolites which provide a highly restricted access
to an egress from its internal structure have a high value

25   for the Constraint Index, and zeolites of this kind usually
have pores of small size, e.g., less than 5 Angstroms. On
the other hand, zeolites which provide relatively free
access to the internal zeolite structure have a low value
for the Constraint Index, and usually pores of large size,

30   e.g., greater than 8 Angstroms. The method by which
Constraint Index is determined is described fully in U.S.
Patent No. 4,016,218, incorporated herein by reference for
details of the method.

A zeolite which may be used in catalyst preparation

35   described herein may be a medium- or large-pore size
zeolite. This zeolite may have a Constraint Index of 12 or

less. Zeolites having a Constraint Index of 2-12 are
generally regarded to be medium-pore size zeolites.
Zeolites having a Constraint Index of less than 1 are
generally regarded to be large-pore size zeolites.
Zeolites having a Constraint Index of 1-2 may be regarded
as either medium- or large-pore size zeolites.

        The members of the class of medium-pore size zeolites
may have an effective pore size of generally from about 5
to about 8 Angstroms, such as to freely sorb normal hexane.
In addition, the structures provide constrained access to
larger molecules. It is sometimes possible to judge from a
known crystal structure whether such constrained access
exists. For example, if the only pore windows in a crystal
are formed by 8-membered rings of silicon and aluminum
atoms, then access by molecules of larger cross-section
than normal hexane is excluded and the zeolite is not of
the medium-pore size type. Windows of 10-membered rings
are preferred, although, in some instances, excessive
puckering of the rings or pore blockage may render these
zeolites ineffective.

        Although 12-membered rings in theory would not offer
sufficient constraint to constitute a medium-size pore, it
is noted that the puckered 12-ring structure of TMA
offretite does show some constrained access. Other 12-ring
structures may exist which may be regarded to be medium-
pore sized, and therefore, it is not the present intention
to classify a particular zeolite solely from theoretical
structural considerations.

        Constraint Index (CI) values for some typical
materials are:

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CI (at test temperature)

ZSM-4	0.5		(316°C)
ZSM-5	6	- 8.3	(371°C-316°C)
ZSM-11	5	- 8.7	(371°C-316°C)
ZSM-12	2.3		(316°C)
ZSM-20	0.5		(371°C)
ZSM-22	7.3		(427°C)
ZSM-23	9.1		(427°C)
ZSM-34	50		(371°C)
ZSM-35	4.5		(454°C)
ZSM-38	2		(510°C)
ZSM-48	3.5		(538°C)
ZSM-50	2.1		(427°C)
TMA Offretite	3.7		(316°C)
TEA Mordenite	0.4		(316°C)
Mordenite	0.5		(316°C)
Clinoptilolite	3.4		(510°C)
Mordenite	0.5		(316°C)
REY	0.4		(316°C)
Amorphous Silica-alumina	0.6		(538°C)
Dealuminized Y (Deal. Y)	0.5		(510°C)
Erionite	38		(316°C)
Zeolite Beta	0.6	- 2.0	(316°C-399°C)

Examples of zeolites having a Constraint Index of from
1 to 12 include ZSM-5, ZSM-11, ZSM-12, ZSM-22, ZSM-23, ZSM-
35, ZSM-38, and ZSM-48.

ZSM-5 is described U.S. Patent Nos. 3,702,886 and Re.
29,948.

ZSM-11 is described in U.S. Patent No. 3,709,979.

ZSM-12 is described in U.S. Patent No. 3,832,449.

ZSM-22 is described in U.S. Patent No. 4,556,477.

ZSM-23 is described in U.S. Patent No. 4,076,842.

ZSM-35 is described in U.S. Patent No. 4,016,245.

ZSM-38 is described in U.S. Patent No. 4,406,859.

ZSM-48 is described in U.S. Patent No. 4,234,231

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Examples of large-pore zeolites, having a Constraint
Index less than 1 include Zeolite Beta, Zeolite Y,
Ultrastable Y (USY), Dealuminized Y (Deal Y), Mordenite,
ZSM-3, ZSM-4, ZSM-10, ZSM-18, and ZSM-20.

5   Zeolite Beta is described in U.S. Patent No. 3,308,069
and Re. No. 28,341.
        ZSM-4 is described in U.S. Patent No. 3,923,639.
        ZSM-10 is described in U.S. Patent No. 3,692,470.
        ZSM-20 is described in U.S. Patent No. 3,972,983.

10   Low sodium Ultrastable Y molecular sieve (USY) is
described in U.S. Patent Nos. 3,293,192 and 3,449,070.
        Dealuminized Y zeolite (Deal Y) may be prepared by the
method found in U.S. Patent No. 3,442,795.
        Zeolite UHP-Y is described in U.S. Patent No.

15   4,401,556.
        Another zeolite which may be used in the present
catalyst is MCM-22, which is described in U.S. Patent Nos.
4,954,325 and 5,107,054.
        A particularly preferred zeolite for use in the

20   present catalyst is zeolite Y.
        Zeolite Y is normally synthesized in forms having
silica:alumina ratios up to about 5:1. These as-
synthesized forms of zeolite Y may be subjected to various
treatments to remove structural aluminum therefrom. Many

25   of these techniques rely upon the removal of aluminum from
the structural framework of the zeolite by chemical agents
appropriate to this end. A considerable amount of work on
the preparation of aluminum deficient faujasites has been
performed and is reviewed in Advances in Chemistry Series

30   No. 121, Molecular Sieves, G.T. Kerr, American Chemical
Society (1973). Specific methods for preparing
dealuminized zeolites are described in the following, and
reference is made to them for details of the method:
Catalysis by Zeolites ,International Symposium on Zeolites,

35   Lyon, Elsevier Sci ntific Publishing Co., (1980)
(dealuminization of zeolite Y with silicon tetrachloride);

U.S. Pat. No. 3,442,795 and G.B. No. 1,058,188 (hydrolysis
and removal of aluminum by chelati n); G.B. No. 1,061,847
(acid extraction of aluminum); U.S. Pat. No. 3,493,519
(aluminum removal by steaming and chelation); U.S. Pat. No.

5   3,591,488 (aluminum removal by steaming); U.S. Pat. No.
4,273,753 (dealuminization by silicon halide and
oxyhalides); U.S. Pat. No. 3,691,099 (aluminum extraction
with acid); U.S. Pat. No. 4,093,560 (dealuminization by
treatment with salts); U.S. Pat. No. 3,937,791 (aluminum·

10   removal with Cr(III) solutions); U.S. Pat. No. 3,506,400
(steaming followed by chelation); U.S. Pat. No. 3,640,681
(extraction of aluminum with acetylacetonate followed by
dehydroxylation); U.S. Pat. No. 3,836,561 (removal of
aluminum with acid); DE-OS No. 2,510,740 (treatment of

15   zeolite with chlorine or chlorine-containing gases at high
temperatures);NL No. 7,604,264 (acid extraction); JA No.
53,101,003 (treatment with EDTA or other materials to
remove aluminum); and J. Catal. 54, 295 (1978)
(hydrothermal treatment followed by acid extraction).

20   Highly siliceous forms of zeolite Y may be prepared by
steaming or by acid extraction of structural aluminum but
because zeolite Y in its normal, as-synthesized condition,
is unstable to acid, it must first be converted to an acid-
stable form. Methods for doing this are known and one of

25   the most common forms of acid-resistant zeolite Y is known
as "Ultrastable Y" (USY); it is described in U.S. Pat. Nos.
3,293,192 and 3,402,996 and the publication, Society of
Chemical Engineering (London) Monograph Molecular Sieves,
186 (1968) by C.V. McDaniel and P.K. Maher. In general,

30   "ultrastable" refers to Y-type zeolite which is highly
resistant to degradation of crystallinity by high
temperature and steam treatment and is characterized by a
R_2O content (wherein R is Na, K or any other alkali metal
i n) of less than 4 weight percent, preferably less than 1

35   weight percent, and a unit cell size less than 24.5
Angstroms and a silica to alumina mole ratio in the range

of 3.5 to 7 or higher. The ultrastable form of Y-type
zeolite is obtained primarily by a substantial reduction of
the alkali metal ions and the unit cell size. The
ultrastable zeolite is identified both by the smaller unit
5   cell and the low alkali metal content in the crystal
structure.

The ultrastable form of the Y-type zeolite can be
prepared by successively base exchanging a Y-type zeolite
with an aqueous solution of an ammonium salt, such as
10   ammonium nitrate, until the alkali metal content of the Y-
type zeolite is reduced to less than 4 weight percent. The
base exchanged zeolite is then calcined at a temperature of
540°C to 800°C for up to several hours, cooled and
successively base exchanged with an aqueous solution of an
15   ammonium salt until the alkali metal content is reduced to
less than 1 weight percent, followed by washing and
calcination again at a temperature of 540°C to 800°C to
produce an ultrastable zeolite Y. The sequence of ion
exchange and heat treatment results in the substantial
20   reduction of the alkali metal content of the original
zeolite and results in a unit cell shrinkage which is
believed to lead to the ultra high stability of the
resulting Y-type zeolite.

The ultrastable zeolite Y may then be extracted with
25   acid to produce a highly siliceous form of the zeolite.

Other methods for increasing the silica:alumina ratio
of zeolite Y by acid extraction are described in U.S. Pat.
Nos. 4,218,307; 3,591,488 and 3,691,099.

In addition to the above-mentioned USY form of zeolite
30   Y, other known forms of zeolite Y, including the rare earth
exchanged Y form (REY), may be used in the present
catalyst.

The zeolite Y used in the present catalyst may have a
unit cell size (UCS) of, for example, 24.5 Angstroms or
35   less, typically 24.15-24.50 Angstroms. Such zeolites

having a low UCS, e.g., of 24.15-24.30 Angstroms, may be
particularly advantageous.

Zeolite Y with a low silanol content may be
manufactured or obtained directly from commercial vendors.

5   The silanol content of zeolites can be adjusted by various
treatments including synthesis, thermal or hydrothermal
treatments as described in the previously cited literature.

The extrudable mass may be passed through an extrusion
die under conditions sufficient to form cylindrical

10   extrudates, which may, in turn, be broken into pellets.

The strength of the extrudate pellets may ultimately
be increased to optimum levels by a calcination procedure.
However, the uncalcined extrudate has sufficient green
strength to withstand the usual handling procedures, which

15   involve drying and possibly ion exchanging and/or
impregnating with sources of hydrogenation components.
Drying of the extrudate pellets may take place at
temperatures of from 100°C to 150°C. This drying procedure
removes water which is physically included or associated

20   with the extrudate. Further water, termed chemically bound
water, may be removed from the extrudate upon calcination
at higher temperatures.

The crush strength of the green strength extrudate
material is improved by a calcination step. This

25   calcination may take place at a sufficient temperature,
e.g., greater than 400°C, for a sufficient time, e.g., at
least 1 hour, in an appropriate atmosphere, e.g., nitrogen
or air. This calcination may cause phase transformation of
the alumina binder to occur. More particularly, the

30   alumina binder may be transformed into the form of gamma-
alumina during this calcination step.

The extrudate catalyst may be combined with a
hydrogenation component or a source of a hydrogenation
component either before or after the calcination step. Th

35   hydrogenation component may be a hydrogenation metal which
may be a noble metal or metals, or a n n-noble metal or

metals. Suitable noble metals include platinum, palladium, and other members of the platinum group such as iridium and rhodium. Suitable non-noble metals include those of Groups VA, VIA and VIIIA of the Periodic Table. The Periodic

5 Table used in this specification is the table approved by IUPAC and the U.S. National Bureau of Standards, as shown for instance in the table of the Fisher Scientific Company, Catalog No. 5-702-10. Preferred non-noble metals are molybdenum, tungsten, cobalt and nickel and combinations of

10 these metals such as cobalt-molybdenum, nickel-molybdenum, nickel-tungsten and cobalt-nickel-tungsten. Metal components may be pre-sulfided prior to use by exposure to a sulfur-containing gas such as hydrogen sulfide at an elevated temperature to convert the oxide form to the

15 corresponding sulfide form of the metal.

The metal may be incorporated into the catalyst by any suitable method such as impregnation or exchange onto the extrudate. The metal may be incorporated in the form of a cationic, anionic or neutral complex such as $Pt(NH_3)_4^{2+}$ and

20 cationic complexes of this type will be found convenient for exchanging metals onto the zeolite. Anionic complexes such as the molybdate or metatungstate ions are useful for impregnating metals into the catalysts.

The amount of the hydrogenation metal is suitably from

25 0.01 to 30 percent by weight, normally 0.1 to 20 percent by weight based on the weight of the zeolite and matrix plus the weight of the hydrogenation metal, although this will, of course, vary with the nature of the component, less of the highly active noble metals, particularly platinum,

30 being required than of the less active base metals.

The catalyst of the invention is particularly useful in hydrocracking, which is typically carried out at a temperature ranging from 250°C (480°F) to 500°C (930°F), preferably from 300°C (570°F) to 450°C (840°F); a hydrogen

35 pressure ranging from 2 to 21 MPa; a liquid hourly space velocity ranging from 0.05 to 10, pr ferably from 0.2 to 3;

a H$_2$ circulation ranging fr m 90 to 1780 Nm^3/m^3 (500 to
10,000 scfb), preferably from 360 to 1070 Nm^3/m^3 (2000 to
6000 scfb).

5   The conversion may be conducted by contacting the
feedstock with a fixed stationary bed of catalyst, a fixed
fluidized bed or with a transport bed. A simple
configuration is a trickle-bed operation in which the feed
is allowed to trickle through a stationary fixed bed. With
such a configuration, it is desirable to initiate the
10   reaction with fresh catalyst at a moderate temperature
which is of course raised as the catalyst ages, in order to
maintain catalytic activity.

The catalyst of the invention may be used to
hydrocrack a variety of feedstocks such as crude petroleum,
15   reduced crudes, vacuum tower residua, coker gas oils, cycle
oils, FCC tower bottoms, vacuum gas oils, deasphalted
residua and other heavy oils. These feedstocks may
optionally be subjected to a hydrotreating treatment prior
to being subjected to the present hydrocracking process.
20   The feedstock, especially in the non-hydrotreated form,
will contain a substantial amount boiling above 260°C
(500°F) and will normally have an initial boiling point of
about 290°C (about 550°F) more usually about 340°C (650°F).
Typical boiling ranges will be about 340°C to 565°C (650°F
25   to 1050°F). Heavy gas oils are often of this kind as are
cycle oils and other non-residual materials. Oils derived
from coal, shale or tar sands may also be treated in this
way. It is possible to co-process materials boiling below
260°C (500°F) but they will be substantially unconverted.
30   Feedstocks containing lighter ends of this kind will
normally have an initial boiling point above 150°C (about
300°F). Feedstock components boiling in the range of 290°
to 340°C (about 550° to 650°F) can be converted to products
boiling from 230°C to 290°C (about 450° to 550°F) but the
35   heavier ends of the feedstock are converted preferentially
to the more volatil components and therefore the lighter

ends may remain unconverted unless the process sev rity is
increased sufficiently to convert the ntire range of
components. A particular hydrocarbon feedstock which may
be used is an FCC recycle oil having an initial boiling
5   point of at least about 343°C (650°F). Other examples of
feedstocks include those with relatively large contents of
non-aromatic hydrocarbons, such as paraffinic feedstocks,
e.g., feedstocks having at least 20 percent by weight,
e.g., at least 50 percent by weight of paraffins.
10   Feedstocks, including those which have been hydrotreated,
which may be used in the present process, include those
having at least 70 wt.% of hydrocarbons having a boiling
point of at least 204°C (400°F).

The hydrocarbon feedstock for the hydrocracking
15   process may be a gas oil. This gas oil may have an initial
boiling point of at least 260°C (500°F), and at least 90
wt.% of the hydrocarbons therein may have a boiling point
greater than 343°C (650°F). This hydrocracking process
involving a gas oil feed may involve a net production of a
20   distillate fraction. For example, the product of the
hydrocracking reaction may have at least 25 wt.% of
hydrocarbons having a distillate boiling range of from 165
to 343°C (330°F to 650°F). The distillate fraction may be
recovered, preferably by a fractional distillation process.

25   **Example 1**
Preparation of High Silica, Low Silanol USY Catalyst
Catalyst A

A commercial high silica USY zeolite containing
essentially no silanol groups as determined by Si-NMR was
30   mulled in a 50/50 wt/wt. mixture with alumina and extruded
to prepare a formed mass. The extruded mass was dried at
120°C (250°F) and calcined for 3 hours in 5 v/v/min.
flowing air at 540°C (1000°F). The calcined product was

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included temperatures from 715-765°F (about 380-410°C), 0.5
LHSV (based on fresh feed relative to total HDT and HDC
catalyst), 4000 scf/bbl (712 n.l.l^{-1}) of once-through
hydrogen circulation, and hydrogen inlet pressure of 815
5   psia (5.61 MPa). The ratio of HDT to HDC catalyst was
typically 1/2, vol/vol.

The feedstock for this Example was a nominal 650-
1050°F (about 345-565°C) Persian Gulf VGO (vacuum gas oil)
having the properties shown in Table 2 below.

10   Table 2
               Persian Gulf VGO Feedstock Properties
       General Properties
       API Gravity   22.0
       Hydrogen, wt.%   12.53
15   Sulfur, wt.%   2.53
       Nitrogen, ppm   780
       Pour point, °F   100
       KV @ 40°C, cSt.   74.34
       KV @ 100°C, cSt.   7.122
20   Composition, wt.%
       Paraffins   24.1
       Naphthenes   22.1
       Aromatics   53.8
       Distillation, °F (°C)
25   IBP   546 (286)
            5%   627 (331)
            10%   664 (351)
            30%   760 (404)
            50%   831 (444)
30   70%   906 (486)
            90%   1003 (539)
            95%   1041 (561)
            EP   1158 (626)

Table 3 shows the improved performance of Catalyst A
35   prepared from low silanol USY compared to Catalyst B. At

equivalent 343°C+ (650°F+) boiling range c nversion,
Catalyst A provides higher yield of valuable distillate
product (165-343°C) with lower yield of light gas (C_1-C_4)
and naphtha (C_5-165°C). Hydrogen consumption is lower due

5   to reduced light gas product. Distillate selectivity,
defined as distillate yield/343°C+ conversion, is 4% higher
for Catalyst A.

Table 3
Hydrocracking Performance with Persian Gulf VGO

		Catalyst A	Catalyst B
Temperature,	°F	755	765
	°C	402	407
650°F+ Conversion, wt.%		40.9	40.7
Yields, wt.%			
H_2S		2.5	2.7
NH_3		0.1	0.1
C_1-C_4		2.0	2.5
C_5-330°F (165°C)		8.7	9.9
330-650°F (145-343°C)		32.7	31.0
650°F+ (343°C)		54.7	54.9
H_2 Consumption, scf/bbl		430	570
(Nm^3/m^3)		76.5	101.5
Distillate Selectivity (Distillate yield/ (650°F) 343°C conversion)		80%	76%

Claims:

1. A process for preparing an alumina b und zeolite
   catalyst, comprising the steps of:
   (a) starting with a zeolite which has a silanol
       content of less than 10%, expressed in terms of
       silicon atoms containing silanol groups vs. total
       silicon atoms;
   (b) mulling together alumina, said zeolite of step
       (a), and water to form an extrudable mass
       comprising an intimate mixture of alumina and
       said zeolite;
   (c) extruding the extrudable mass of step (b) to form
       a green strength extrudate; and
   (d) calcining the green strength extrudate of step
       (c) to increase the crush strength of the
       extrudate.

2. A process according to claim 1, wherein said green
   strength extrudate is calcined at a temperature of at
   least 400°C in calcination step (c).

3. A process according to claim 1 or claim 2, wherein
   said alumina, which is introduced into mulling step
   (a), is in the form of pseudoboehmite.

4. A process according to any preceding claim, wherein
   said green strength extrudate of step (b) is dried to
   remove physically included water therefrom prior to
   calcination step (c).

5. A process according to claim 5, wherein the drying of
   the extrudate prior to step (c) takes place at a
   temperature of 100°C to 150°C.

6. A process according to any preceding claim, wherein
   said zeolite is a large-pore size zeolite.